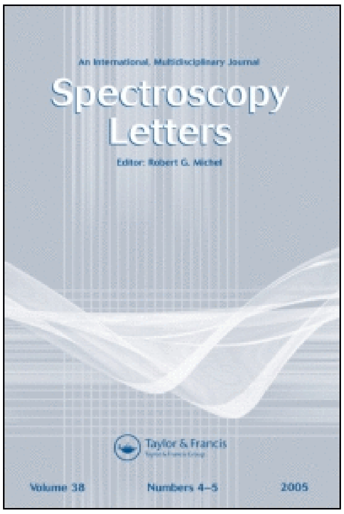

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Natural Abudance ^{17}O NMR Studies of Thiol Esters and Related Analogs

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NATURAL ABUNDANCE ^{17}O NMR STUDIES OF THIOL ESTERS AND RELATED ANALOGS

KEY WORDS: ^{17}O NMR spectroscopy, thiol esters, esters

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ABSTRACT

Natural abundance ^{17}O NMR data for a series of thiol esters and related analogs are reported. The carbonyl signal of the thiol esters range from 463 ppm to 514 ppm; these values are downfield of their oxygen analogs by ca. 150 ppm. A linear relationship between the ^{17}O NMR chemical shift of the thio-compounds and their oxo-analogs is observed.

INTRODUCTION

^{17}O NMR spectroscopy has emerged as a sensitive method for assessment of the effect of structural variation on functional group properties.[1,2] Divalent sulfur and divalent oxygen compounds are similar in bonding and properties; however, the study of the differences in properties of thio- and oxo-organic compounds represent an area of intensive investigation.[3,4] Thiol esters are examples of divalent sulfur compounds which have been studied in detail, in part, due to the important role thiol esters (e.g., acetyl-CoA) play in biochemistry.[5] The carbonyl oxygen signal as well as the single bond oxygen signal of esters has been found to be influenced by structure modification of either part of the ester functional group.[6-12] Quantitative relationships between torsion angles and ^{17}O NMR chemical shifts have been reported for aryl esters.[13] During a recent investigation of the ^{17}O NMR spectroscopic characteristics of lactones we observed striking downfield chemical shifts for the carbonyl group signal of two thiobutyrolactones compared to the carbonyl signal of their fully oxygenated counterparts.[14] We report here an investigation which more broadly examines the effect on the ^{17}O NMR chemical shift of the carbonyl group of esters on replacing an oxygen atom with a sulfur atom.

RESULTS

The ^{17}O NMR chemical shift data, at natural abundance, for thiol esters, their ester counterparts and related thio substituted compounds obtained in acetonitrile solution at 75°C are reported in Table 1. The carbonyl signal of the thiol esters ranges from 463 ppm for the thiolactone **14** to 514 ppm for the aryl thioacetates **16** and **18**. The carbonyl group ^{17}O NMR chemical shifts for the thiol esters appear significantly downfield from their ester analogs, typically by 150 ppm (cf. **1** to **2** and **15** to **16**). The effect of changing substitution adjacent to the carbonyl group on the carbonyl chemical shift appears to be essentially the same in both esters and thiol esters. For example, the carbonyl signal of methyl butyrate **7** is upfield of that of methyl acetate **1** by 6 ppm; similarly, the carbonyl signal of methylthiobutyrate **8** is also upfield of methylthioacetate **2** by 6 ppm. Also note that the carbonyl signal of ethyl propionate is upfield of that of ethylacetate by 10 ppm and the carbonyl signal for ethylthiopropionate is upfield of that of ethylthioacetate by 9 ppm.

TABLE 1
^{17}O NMR Data for Esters, Thiol Esters and Related Compounds in Acetonitrile at 75°C.

No.	*Compound*	*δ(C=O)*	*δ(-O-)*
1	CH_3COOCH_3	361	141.2
2	$CH_3COSCH3$	511	--
3	$CH_3COOCH_2CH_3$	363	169
4	$CH_3COSCH_2CH_3$	511	--
5	$CF_3COOCH_2CH_3$	351.5	162
6	$CF_3COSCH_2CH_3$	508.7	--
7	$CH_3CH_2CH_2COOCH_3$	355.5	138.3
8	$CH_3CH_2CH_2COSCH_3$	505	--
9	$CH_3CH_2COOCH_2CH_3$	353	167.8
10	$CH_3CH_2COSCH_2CH_3$	502.4	--
11	butyrolactone[b]	340.5	178.5
12	thiobutyrolactone[b]	494.3	--
13	2(5H)Furanone[b]	326.7	172.7
14	2(5H)Thiophenone[b]	462.7	--
15	phenyl acetate	370	201.3
16	phenyl thioacetate	513.7	--
17	p-tolyl acetate	369	199.5
18	p-tolyl thioacetate	513.7	--
19	3,4-Benzocoumarin	339	205
20	6H-Dibenzo(b,d)thiopyran-6-one	462	--
21	PhNHCOO-nBu	244	122
22	PhNHCOS-nBu	340	--
23	$CH_3COOCOCH_3$[c]	411	273
24	$CH_3COSCOCH_3$	546	--
25	$EtOOCCH_2COOEt$	362.8	173
26	$EtOOCCH_2CSOEt$	360.7	244.3, 172.4
27	$PhNHCOOCH_3$	245	96
28	$PhNHCSOCH_3$	--	143.5

(a) Data obtained at natural abundance on 0.5 M solutions; 1% 2-butanone (558±1 ppm); (b). Data taken from ref. 14; (c) Data taken from ref. 18.

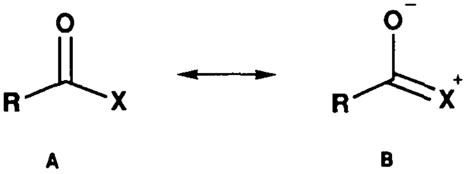
The effect on the carbonyl signal by structural changes on singly-bonded oxygen for esters is small.[9-12] Changes in substituent on the sulfur atom of thiol esters appear to affect the carbonyl signal even less than the same change for esters. This result is illustrated by the fact that the carbonyl signal for ethylacetate **3** is deshielded by 2 ppm from that of methylacetate **1** whereas the two analogous thiol esters **2** and **4** have the same chemical shifts.

A representative example of substitution of singly-bonded oxygen by sulfur in urethanes is provided by **21** and **22** and a significant downfield shift of 96 ppm is noted for the carbonyl oxygen signal for this class of compounds. Similarly, in another class of carbonyl compounds, replacement of the singly-bonded oxygen by sulfur of an anhydride causes a large downfield shift of ca. 135 ppm (compare **23** and **24**).

Examples of the effect of replacing a carbonyl oxygen with sulfur on the ^{17}O chemical shift of the singly-bonded oxygen in an ester and a urethane are also included in Table 1. Comparison of the values for diethylmalonate **25** and its thion derivative **26** reveals that a downfield shift of ca. 71 ppm for the signal of the singly-bonded oxygen occurs. A downfield shift of 47 ppm for the singly-bonded oxygen signal is noted as a result of the presence of a thio carbonyl group in the urethane system; compare **27** and **28**.

DISCUSSION

Some properties of thiol esters resemble ketones more than that of oxygen esters. For example, the carbonyl infrared stretching frequencies[4,15] and carbonyl carbon ^{13}C chemical shifts[16] are near the regions observed for ketones. Similarly, the ^{17}O NMR chemical shifts of the thiol esters (ca. 500 ppm) reported here are closer to the values for analogous ketones (ca. 550 ppm) than to the analogous esters (ca. 350 ppm). The relative position of the carbonyl group ^{17}O NMR chemical shift of ketones, acid chlorides, esters and amides has been discussed and the contribution from the mesomeric form **B** is considered critical.[11,17]



Upfield chemical shifts of the carbonyl signals of esters and amides are considered related to significant contributions from **B**.[11,17] The downfield position of the chemical shift of simple thiol esters (e.g., **2**, **4** and **8**) relative to oxygen esters (e.g., **1**, **3** and **7**) is consistent with greater contribution from A in the thiol esters compared to their oxygen counterparts.

The factors influencing the carbonyl ^{17}O NMR chemical shift in the thiol esters are shown to be similar to those for the oxygen esters by the plot given in

Figure 1. A good correlation (r=0.99) is observed from the plot of the carbonyl chemical shift values of the thiol esters versus those for the oxygen esters. The plot in Figure 1 includes data for each thio-oxy pair given in Table 1. The results for the pairs of simple esters **1-20** fall in a rather narrow range of chemical shifts; however, inclusion of the urethane pair **21-22** and the anhydride set **23-24** extends the range considerably. Plotting of the data for the thion pairs **25-26** and **27-28** not only increases the range but a good correlation is maintained. For these latter two pairs the ^{17}O chemical shift data being plotted is for the singly-bonded oxygens of the esters (**25-26**) and the urethanes (**27-28**). Frequently, doubly- and singly-bonded oxygen chemical shifts respond differently to structure variation. However, in this case it is probably not fortuitous that the singly-bonded oxygen

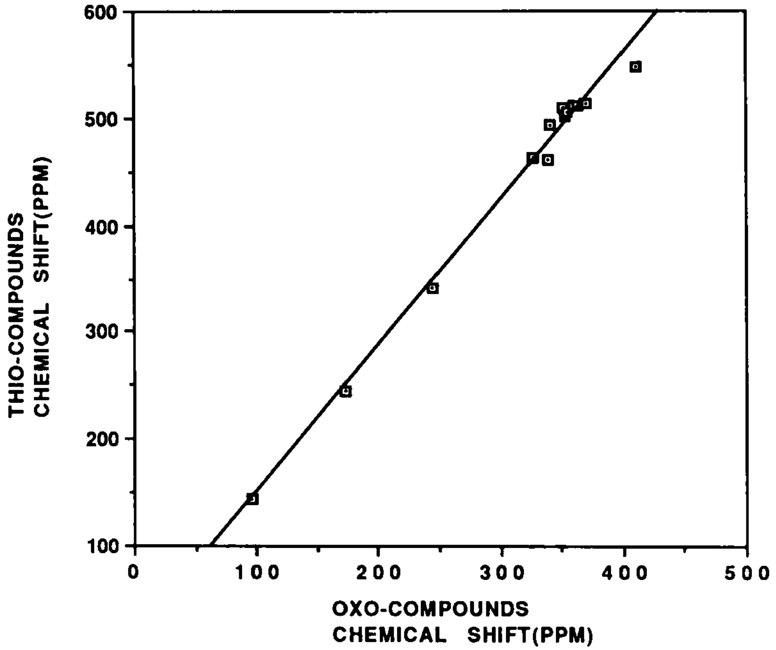


FIGURE 1. PLOT OF O-17 NMR CHEMICAL SHIFTS OF THIOL ESTERS AND ANALOGS VS 17-O NMR CHEMICAL SHIFTS OF RELATED ESTERS AND ANALOGS.

chemical shifts fall on the line in Figure 1 since in these ester and related functional groups the singly-bonded oxygen atoms are, by resonance, an integral part of the function group.

It is clear that ^{17}O NMR spectroscopy is a sensitive tool for the study of structure and bonding in thiol esters and related compounds. The differences in the chemical shift of esters and thiol esters are large (ca. 150 ppm) and thus ^{17}O NMR has the potential for use as a probe in mechanistic studies involving direct comparisons between acyl and thioacyl reactivities.

EXPERIMENTAL

The compounds used in this study were commercially available from Aldrich and/or Lancaster. The ^{17}O NMR spectra were recorded on a Varian VXR-400 spectrometer equipped with a 10 mm broad-band probe. All spectra were acquired at natural abundance, at 75°C in acetonitrile (Aldrich, anhydrous gold label under nitrogen) containing 1% 2-butanone as an internal standard. The concentration of the compounds employed in these experiments was 0.5 M. The signals were referenced to external deionized water at 75°C. The 2-butanone resonance (558±1 ppm) was used as an internal check on the chemical shift measurements for these compounds. The instrumental settings were: spectral width 35 kHz, 2K data points, 90° pulse angle (40 ms pulse width), 200 ms acquisition delay, 29 ms acquisition time, and 20,000-40,000 scans. The spectra were recorded with sample spinning and without lock. The signal-to-noise ratio was improved by applying a 25 Hz exponential broadening factor to the FID prior to Fourier transformation. The data point resolution was improved to ±0.1 ppm by zero filling to 8K data points. The reproducibility of the chemical shift data is estimated to be better than ±1.0 pppm.

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